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MAGNETIC AND MICELLAR EFFECTS IN PHOTOREACTIONS. ^{13}C NMR DETERMINATION OF SELECTIVE ^{13}C ENRICHMENT IN A DIBENZYL KETONE PHOTOPRODUCT.

N.J. Turro and C.-J. Chung, Department of Chemistry, Columbia University
New York, New York 10027

R.G. Lawler* and W.J. Smith, III, Department of Chemistry, Brown University
Providence, Rhode Island 02912

ABSTRACT

The photolysis of dibenzyl ketone (DBK) in micellar solution results in formation of 1-phenyl-4-methyl acetophenone (PMAP) as a minor product; quantitative integration of the ^{13}C NMR spectrum of PMAP produced by photolysis of DBK in micellar solution demonstrates that significant selective ^{13}C enrichment has occurred at three carbon atoms.

INTRODUCTION. Considerable evidence has been presented to support the postulate that the photolysis of dibenzyl ketone (DBK) in micellar solution[1] proceeds by the mechanism shown in Figure 1. Two combination pathways have been observed for the primary, geminate triplet radical pair (^3D) after intersystem crossing (ISC) to a singlet radical pair (^1D) to regenerate DBK (path a, Figure 1), or to produce the isomeric ketone, 1-phenyl-4-methylacetophenone (PMAP).[2] Both DBK and PMAP have been shown[2] to be significantly enriched in ^{13}C at the carbonyl carbon relative to the initial DBK. It has been proposed that this enrichment is due to a magnetic isotope effect on the ISC step. If this is true, the ^{13}C enrichment at each carbon in the recombination products will vary in a manner that is related to the magnitude of the ^{13}C electron-nuclear hyperfine coupling constant, a_c, for the corresponding carbon in the benzyl-phenylacetyl radical pair (D).

Table 1 lists the measured, or estimated, values of a_c for the 11 different carbons in D (see Figure 2 for numbering system). If, as expected for freely diffusing radical pairs,[3] the ^{13}C enrichment increases monotonically with a_c, it is apparent from Table 1 that the ordering of ^{13}C enrichment should be $C_1 > C_{10} > C_{11} > C_{aromatic}$. Evidence to support this prediction is found in the observation[1], made using specifically ^{13}C-labelled DBK, that the α-carbon ($C_{10}+C_{11}$) of DBK (recovered after partial photolysis) is enriched to a lesser extent than the carbonyl carbon (C_1). DBK enrichments have the disadvantage, however, that, for all except C_1, they combine the effects of a_c on both halves of the radical pair. In an effort to avoid this source of ambiguity we have undertaken a quantitative measurement of the enrichment at each carbon in PMAP.

METHODS AND RESULTS. Although mass spectrometric analysis (ms) allows determination of the global ^{13}C enrichment in PMAP, the measurement of ^{13}C enrichment at each carbon is best made by a magnetic resonance method. ^1H NMR ^{13}C satellite intensities were, for example, employed as a complement to ms for monitoring the ^{13}C content of specifically labelled DBK and PMAP samples.[1] Furthermore, ^{13}C NMR possesses the advantage that specific ^{13}C labelling is not required, since small deviations from natural abundance may be determined directly by comparing peak intensities from the sample of interest with those from a standard.[4] The relative enrichments for PMAP obtained in this way are summarized in Table 1.

A typical run was made as follows: the micellar photolysis of DBK was carried out to ca.

80% completion in the ordinary manner.[5] The 5-10% PMAP formed from the photolysis was isolated by preparative glpc. Inasmuch as quantitative analysis by ^{13}C NMR is a relatively new method[6] for which standard protocols seem to be lacking, the method employed to determine ^{13}C enrichment is detailed below.

The relative ^{13}C enrichments given in Table 1 were obtained with a Bruker WM-250 NMR spectrometer operating at 62.8 MHz using solutions containing 110 mg PMAP in 1.5 ml $CDCl_3$.[7] In a single spectrometer session, spectra were obtained both from the sample of PMAP isolated from photolysis and from a standard sample of PMAP (prepared by addition of p-tolylmagnesium bromide to phenylacetaldehyde followed by oxidation of the resulting alcohol with chromic anhydride). The comparison of samples, rather than simple computation of relative peak areas within a single spectrum, was essential in order to minimize systematic frequency-dependent intensity errors of the order of 5% introduced by the spectrometer. The enrichments, S, reported in Table 1 are therefore "isotope ratios" in the same sense that the term is employed in mass spectrometry.[8]

The ^{13}C NMR spectra of these samples were obtained using inverse gated decoupling to suppress the NOE,[9] and a pulse angle of 90° to maximize the intensity per pulse and make the effects of relaxation easily predictable. The time between pulses, 150 seconds, was selected to be 5 times the longest carbon T_1 (ca. 30 sec. for carbons 1 and 4) as determined by the progressive saturation method. Under these conditions less than 1% distortion of any peak is expected due either to the NOE or incomplete relaxation between pulses.

Although most of the carbon peaks were well resolved in proton decoupled spectra at 62.8 MHz four of the aromatic carbon peaks, 5-8, occur in pairs separated by only 7 Hz. It was, therefore, necessary to apply two special data processing techniques to assure baseline separation of these peaks: (a) The 16K FID was zero-filled[10] to 256 K and processed using a disk-based extended FT program supplied by Bruker. This enabled a data point resolution of 0.1 Hz, i.e., ca. 5% of the linewidth, to be achieved. (b) The lineshape was transformed from Lorentzian to Gaussian.[11]

TABLE 1. RELATIVE ^{13}C ISOTOPE RATIOS FOR PMAP BY ^{13}C NMR.

Carbon No.[a]	δ_c(ppm)[b]	S[c]	a_c(Gauss)
1	197.40	1.23 ± .01[d]	+124[e]
2	144.12	(1.00)	-14[f]
3	134.93	0.99	0
4	134.25	0.99	+11[g]
5	129.59	0.99	0
6	129.48	1.01	+12[g]
7	128.91	0.99	-9[g]
8	128.79	0.99	0
9	126.95	0.98	0
10	45.60	1.17	+51[e]
11	21.84	1.06	+24[f]

(a) See Figure 2 for number system.
(b) Chemical shifts relative to $\delta_c^{CDCl_3}$ = 77.27 ppm. Assignments made using selective ^1H decoupling.
(c) Ratio of ^{13}C NMR intensities for analytical and standard samples divided by the ratio for C_2.[7]
(d) Error estimate of 1% is one standard deviation and represents maximum difference of ratios obtained by curve fitting and spectrum subtraction. See text.
(e) H. Paul and H. Fischer, Helv. Chim. Acta, 56, 1575 (1973).
(f) A.M. Ihrig, P.R. Jones, I.N. Jung, R.V. Lloyd, J.L. Marshall and D.E. Wood, J. Am. Chem. Soc. 97, 4477 (1975).
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The ratio of intensities of the 11 well-resolved lines in the analytical and standard PMAP samples were determined by two methods: (1) Each of the 11 pairs of peaks was fit to a Gaussian function using a least squares subprogram. 60 data points were employed for each peak. The relative areas were assumed to be proportional to the product of the best-fit peak amplitudes and widths. (2) The spectrum of the standard sample was multiplied by a scale factor and subtracted from the spectrum of the analytical sample. The difference was displayed using a dual display routine and the scale factor was adjusted for each peak until the maximum cancellation of the peaks was achieved. The relative scale factors were thus a measure of the relative intensities of the peaks in the two spectra.

Figure 2A shows the 11 lines from the analytical sample as they appeared after zero-filling and Gaussian convolution. The number over each peak is its isotope ratio (see Table 1). Figure 2B shows the difference between the analytical and standard spectra using a common scale factor chosen to be the average of those required to obtain cancellation of peaks 2-9, i.e., the aromatic carbons, all of which, in any case, are the same within ca. 2%. The oscillations in the difference spectrum for peaks 2-9 arise from small mismatches in lineshape or line position between the analytical and standard samples. Note, however, that the net areas of the difference peaks are nearly zero, i.e., the areas above and below the baseline are nearly equal.

DISCUSSION. The data in Table 1 may be summarized as follows: (a) statistically significant enrichments are obtained for C_1, C_{10}, and C_{11} in the expected order $C_1 > C_{10} > C_{11}$, and (b) the ^{13}C contents of the other 8 carbons varied in this particular sample by less than 2% from those of the natural abundance standard. The enrichment, S, seems, however, to depend somewhat non-linearly on a_c. For example, C_{10} seems to be over-enriched and C_2 under-enriched relative to the magnitudes of their -yperfine couplings. The data are, nevertheless, in good qualitative agreement with the expectations for a predominant nuclear spin, rather than mass, isotope effect for the formation of PMAP. A more quantitative interpretation of the data will require comparisons with ^{13}C enrichments in DBK isolated from the same sample as well as development of a specific theoretical model for spin dynamics during radical pair reactions in micelles. Such studies are presently in progress.

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7. Preliminary ^{13}C NMR measurements at 62.8 MHz were carried out over a period of several months using a 300 mg sample of PMAP containing 5% DBK and 10% diphenylethane (DPE) (by ^{13}C NMR). The sample whose analysis is given in Table 1 was obtained by recrystallizing this larger batch from 95% ethanol until it contained ca. 0.3% DBK and 1% DPE (by ^{1}H NMR). The earlier measurements explored a variety of methods for suppressing relaxation and NOE effects, including the addition of up to 0.03 M $Cr(acac)_3$ and removal of broadband proton decoupling. The resolution under these conditions was, however, insufficient to distinguish carbons 5-8 from each other and from the impurities. Nevertheless, the intensity ratios for the other seven lines, averaged over 8 separate sets of spectra, deviated at most by 4% from those shown in the Table.
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Figure 1. The Conventional Mechanism for Photolysis of DBK in Micellar Solutions.

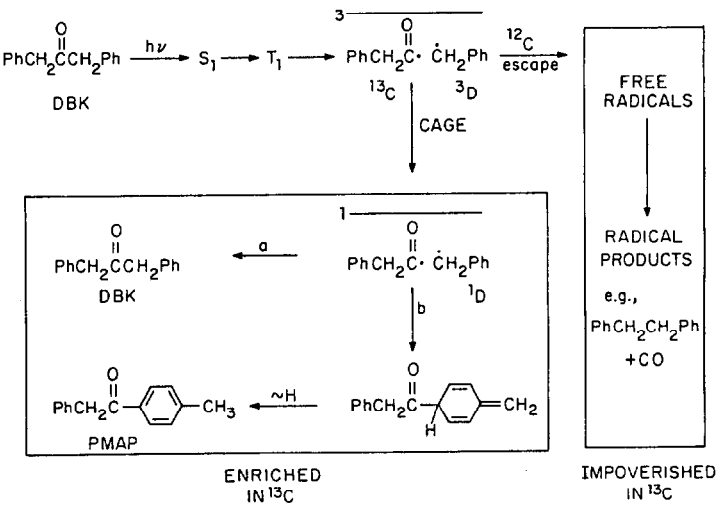
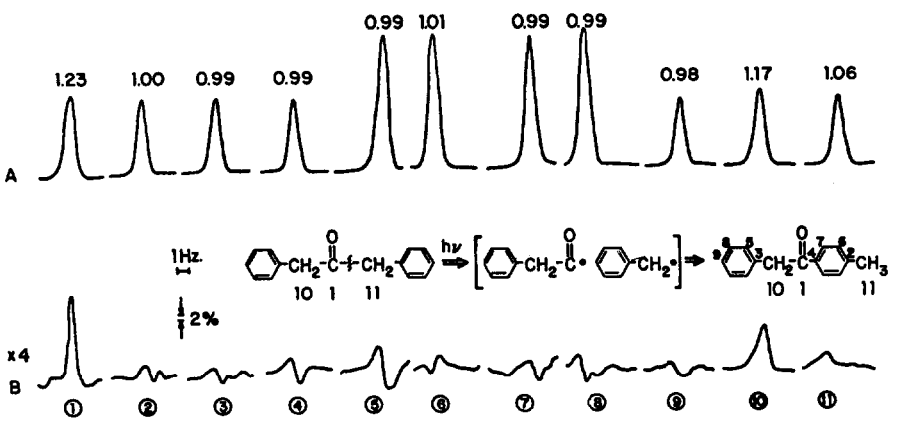


Figure 2. (A) NMR Peaks of PMAP After Zero-Filling and Gaussian Convolution.
(B) Difference Between Analytical and Standard Spectra. See text for discussion.



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